

Japanese Patent Laid Open No. 307146/1995 (or JP7-307146)

Laid Open: November 23, 1995

Application No. 98395/1994

Filing Date: May 12, 1994

Applicant: Ube Industries, Ltd.

Inventors: Hiroshi Kurauchi, et al.

Title of the Invention

Battery Separator and Preparing Same

[Summary]

[Object]

The present invention relates to a battery separator comprising a porous laminate film having a fine and uniform pore diameter, also having a moderate pore-closing start temperature, a high upper-limit temperature to maintain the pore closure condition, a wide temperature range to maintain the pore closure condition, and a high peel strength, and capable of remedying the drawbacks of conventional pore laminate films, as well as a process for preparing the same.

[Construction]

The present invention is concerned with a battery separator comprising a porous laminate film obtained by stretching a laminate film of three or more alternate layers of polypropylene and polyethylene to thereby render the film porous, as well as a process for preparing the same.

[Claims]

1. A battery separator comprising a porous laminate film obtained by stretching a laminate film of three or more alternate layers of polypropylene and polyethylene to thereby render the film porous.

2. A battery separator comprising a porous laminate film having a maximum pore diameter of 0.02 to 2 μm , a porosity of 30 to 80%, an interlaminar peel strength of 3 to 60 g/15 mm, a pore-closing start temperature of 135 to 140°C, and an upper-limit temperature of 180 to 190°C to maintain the pore closure condition, said porous laminate film being obtained by stretching a laminate film of three or more alternate layers of polypropylene and polyethylene, the polypropylene and polyethylene layers being laminated in the order of polypropylene layer, polyethylene layer and polypropylene layer, to thereby render the film porous.

3. A process for preparing a battery separator, which process comprises heat-treating a laminate film of three or more layers at a temperature of 110 to 140°C, said laminate film having been obtained by thermocompression bonding of polypropylene and polyethylene films at a temperature of 120 to 140°C, thereafter stretching the thus heat-treated film by 5 to 200% while holding the film at a temperature of -20°C to +50°C, then stretching the thus-stretched film by 100 to 400% while holding the film at a temperature of 70 to 130°C, and subsequently heat-treating the thus-stretched film at a temperature higher by 5 to 45°C than the temperature of the latter stretching step.

4. A process for preparing a battery separator, which process comprises heat-treating a laminate film of three or more layers at a temperature of 110 to 140°C, said film having been obtained by thermocompression bonding of polypropylene and polyethylene films in an alternate manner

at a temperature of 120 to 140°C, thereafter stretching the thus heat-treated film by 10 to 100% while holding the film at a temperature of 20 to 35°C, then stretching the thus-stretched film by 100 to 400% while holding the film at a temperature of 70 to 130°C, and subsequently heat-treating the thus-stretched film at a temperature higher by 5 to 45°C than the temperature of the latter stretching step to obtain a porous laminate film having a maximum pore diameter of 0.02 to 2 μ m, a porosity of 30 to 80%, an interlaminar peel strength of 3 to 60 g/15 mm, a pore-closing start temperature of 135 to 140°C, and an upper-limit temperature of 180 to 190°C to maintain the pore closure condition.

5. A process for preparing a battery separator as set forth in Claim 3 or Claim 4, wherein the polypropylene film has a birefringence of 10×10^{-3} to 20×10^{-3} and exhibits an elastic recovery of 80 to 94% at 100% elongation after heat treatment at 150°C for 30 minutes, while the polyethylene film has a birefringence of 20×10^{-3} to 40×10^{-3} and exhibits an elastic recovery of 20 to 50% at 50% elongation.

[Detailed Description of the Invention]

[Field of the Invention]

The present invention relates to a safe and reliable battery separator having a high peel strength and tensile modulus, a fine and uniform pore diameter, and a wide temperature range to maintain a thermal pore closure condition, as well as process for preparing such film. More particularly, the invention is concerned with a battery separator obtained by stretching a laminate film of three or more polypropylene and polyethylene layers to render the film porous.

[Prior Art]

With the recent technological advance there has been an increasing demand for high precision films for various purposes in various fields, and the use of a porous laminate film as a battery separator has been proposed.

Reference will now be made to the battery as an example. In the battery, a separator is interposed between positive and negative electrodes for the prevention of short-circuit. Recently, a non-aqueous electrolyte battery such as a lithium battery, especially a lithium secondary cell, high in both energy density and electromotive force and with reduced self-discharge, has come to be developed and put into practical use. As examples of negative electrode materials in the lithium battery are known metal lithium, alloys of lithium and other metals, organic materials such as carbon or graphite capable of adsorbing lithium ion or capable of storing lithium ion by intercalation, and electrically conductive polymers doped with lithium ion. Known as positive electrode materials are, for example, graphite fluoride represented by $(CF_x)_n$, metal oxides such as MnO_2 , V_2O_5 , CuO , Ag_2CrO_4 and TiO_2 , sulfides, and chlorides. As a non-aqueous electrolyte solution there is used a solution of an electrolyte such as $LiPF_6$, $LiBF_4$, $LiClO_4$, or $LiCF_3SO_3$, in an organic solvent such as ethylene carbonate, propylene carbonate, γ -butyrolactone, acetonitrile, 1,2-dimethoxyethane; or tetrahydrofuran. However, lithium is very reactive, so in the event of flowing of an abnormal electric current due to external short-circuit or erroneous connection, it is likely that a remarkably increased battery temperature

will cause a thermal damage to a device equipped with the lithium battery. In order to obviate such danger, such various porous films have heretofore been proposed as separators.

① Porous single-ply film of a thermoplastic resin such as polyethylene or polypropylene (see, for example, Japanese Patent Publication Nos. JP46-40119B, JP55-32531B and JP59-37292B, Japanese Patent Provisional Publication Nos. JP60-23954A and JP2-75151A, and USP 3,679,538).

② Porous film of a mixture of polyethylenes different in molecular weight or a mixture of polyethylene and polypropylene (see, for example, Japanese Patent Provisional Publication Nos. JP2-21559A, JP2-334309A and JP5-331306A).

③ Porous film using, as a support, a thermoplastic resin or a non-woven fabric (see, for example, Japanese Patent Provisional Publication Nos. JP3-245457A and JP1-258358A).

④ Porous laminate film constituted by a laminate of plural porous films of different thermoplastic resins (see, for example, Japanese Patent Provisional Publication Nos. JP62-10857A and JP63-308866A) Japanese Patent Publication No. JP3-65776B and Japanese Patent Provisional Publication No. JP6-20671A).

⑤ Porous laminate film made by combining two porous films via adhesive or by application of heat and pressure.

The use of these porous single-ply or laminate films as separators basically intends to prevent short-circuit between both electrodes, keep the battery voltage constant, close the pores upon increase in internal temperature of the battery beyond a predetermined level due to the flow of an abnormal electric current for example, to increase the electric

resistance so as to prevent the flow of ion between both electrodes, and thereby terminate the battery function to prevent the danger of fire, etc. caused by an excessive rise of temperature and ensure safety. The danger preventing function in an excessively elevated temperature condition is an extremely important function of the separator for battery, which function is generally called "pore closing" or "shutdown (SD)."

In the present invention, the temperature at which the gas permeation rate (Gurley value: see/100cc) exceeds 6,000 is designated "pore-closing start temperature" or "SD start temperature." As to the gas permeation rate, it will sometimes be referred to below also as percent gas permeation. In the separator for battery, a too low pore-closing start temperature involves a problem in point of practical use because the flow of ion is prevented by a slight rise of temperature, and a too high pore-closing start temperature also involves a problem in point of safety because it is likely to cause fire, etc. in the case where the battery is a lithium battery for example. Generally considered suitable as the pore-closing start temperature is a temperature in the range of 110 to 160°C, preferably 120 to 150°C. In the present invention, moreover, an upper-limit temperature to maintain the pore closure or shutdown condition is designated pore closure maintaining upper-limit temperature or heat-resisting temperature, and the temperature range or width from the pore-closing start temperature or SD start temperature up to the heat-resisting temperature is designated pore closure maintaining temperature range or heat-resisting temperature width. In a battery using a porous film as a separator, if the

internal temperature of the battery rises beyond the pore closure maintaining upper-limit temperature, the film will be cut thermally and ruptured, thus resulting in loss of the pore closure condition, again permitting the flow of ion and a separator for battery is required to have an appropriate pore-closing start temperature, a high pore closure maintaining upper-limit temperature and a wide pore closure maintaining temperature range. The separator for battery is further required to be low in electric resistance, high in mechanical strength such as tensile modulus and small in variations such as variations in thickness and electric resistance, in addition to meeting the aforesaid pore-closing characteristics.

[Problems to be Solved by the Invention]

Various porous films have been proposed like the foregoing films (1) to (5), but according to studies of the present inventors, for example the porous single-ply film of polypropylene as a separator for battery is disadvantageous in that its pore-closing start temperature, which is about 170°C or higher, is close to the melting point of lithium, while the porous single-ply film of polyethylene has an appropriate pore-closing start temperature of 170°C or so, but its pore closure maintaining upper-limit temperature is about 145°C and thus the pore closure maintaining temperature range thereof is too narrow, further, since the tensile modulus thereof is low, elongation is apt to occur in the battery manufacturing process and thus a difficulty is encountered also in point of productivity. Thus, in point of safety, a further improvement is required of the porous single-ply films of thermoplastic resins.

The porous film of a mixture of polyethylenes different in molecular weight has a pore closure maintaining upper-limit temperature of about 150°C and a tensile modulus of

about 3,400 kg/cm², which are only slightly higher than those of the foregoing porous single-ply film of polyethylene. A porous film of a sea-island structure obtained by stretching a mixture of polyethylene and polypropylene has a pore closure maintaining upper-limit temperature of about 180°C and a tensile modulus of about 4,200 to 6,400 kg/cm², thus exhibiting improvement in SD function and mechanical properties over the polyethylene mixture film, which improvement, however, is still unsatisfactory. Moreover, the sea-island structure formed by stretching the polyethylene-polypropylene mixture is apt to cause variations in point of quality, and reproducibility is low.

The porous film on a support of non-woven fabric or the like is unsatisfactory in point of safety, which is attributable to the non-woven fabric or the like, besides also as to its pore closure maintaining function, improvement is required in point of reliability at high temperatures as is the case with the aforesaid porous film of polyethylene or polypropylene.

As to the porous laminate film constituted by a laminate of plural porous films of different thermoplastic resins, it is prepared by stretching two kinds of films of different materials to make them porous, then putting one on the other, and subsequent stretching and the other, and subsequent stretching and compression bonding or adhesion using an adhesive. Theoretically, the resulting porous laminate film ought to have the characteristics required of the separator for battery. Actually, however, the pore positions of one film and those of the other film are in many cases deviated from each other at the time of combining the two, resulting in that the

pores on the surface side of the laminate are not in communication with the pores on the back side of the laminate, and hence the porous laminate film obtained is apt to increase in its electric resistance. Besides, the laminate film is easily curled or wrinkled. Since the constituent films have been made porous, it may be difficult to combine the two, but if both films are subjected to compression bonding or adhesion strongly at a high temperature, their pores will be crushed to the extent of losing their function as porous films, thus resulting in increase of electric resistance. On the other hand, if compression bonding or adhesion is made lightly to maintain the function as porous films, there will occur delamination, wrinkling, or elongation, of the films at the time of mounting the laminate film as separator into a battery because of a low peel strength, and thus there remains a problem in point of quality of the battery. In the case of stretching porous films in a superimposed state of one on the other, not only there will be an increase in the number of manufacturing steps as a basic problem but also the above-mentioned problems are apt to occur more or less, and Gurley value is low, so there still remains room for improvement in the case where the resulting laminate film is to be used as a separator for battery.

The present inventors have already proposed as a separator for battery a porous single-ply film (e.g. Japanese Patent Publication No. JP2-11620B) and a porous laminate film constituted by a laminate of a porous polyethylene film and a porous polypropylene film (Japanese Patent Provisional Publication No. JP6-20671A). But in view

of the above-mentioned points the present inventors later made studies for the purpose of developing a porous film battery separator, especially a battery separator comprising a thermoplastic, porous, laminate film having a fine and uniform pore diameter, a moderate pore-closing start temperature, a high pore closure maintaining upper-limit temperature, a wide pore closure maintaining temperature range, and high peel strength and elastic modulus, and capable of remedying the drawbacks of the conventional porous laminate films. As a result we accomplished the present invention.

[Means for Solving the Problems]

The present invention relates to a porous laminate film obtained by stretching a laminate film of three or more alternate layers of polypropylene and polyethylene to render the film porous.

The present invention also relates to a battery separator comprising a porous laminate film having a maximum pore diameter of 0.02 to 2 μ m, a porosity of 30 to 80%, an interlaminar peel strength of 3 to 60 g/15 mm, a pore-closing start temperature of 35 to 140°C, and a pore closure maintaining upper-limit temperature of 180 to 190°C, the porous laminate film being obtained by stretching a laminate film of three or more alternate layers of polypropylene and polyethylene, the polypropylene and polyethylene layers being laminated in the order of polypropylene layer, polyethylene layer and polypropylene layer, to render the film porous.

The present invention further relates to a process for preparing a battery separator, which process comprises

heat-treating a laminate film of three or more layers at a temperature of 110 to 140°C, the said laminate film having been obtained by thermocompression bonding of polypropylene and polyethylene films at a temperature of 120 to 140°C, thereafter stretching the thus heat-treated film by 5 to 200% while holding the film at a temperature of -20°C to +50°C, then stretching the thus-stretched film by 100 to 400% while holding the film at a temperature of 70 to 130°C, and subsequently heat-treating the thus-stretched film at a temperature higher by 5 to 45°C than the temperature of the latter stretching step.

The present invention is further concerned with a process for preparing a battery separator comprising a porous laminate film having a maximum pore diameter of 0.02 to 2 μ m, a porosity of 30 to 80%, an interlaminar peel strength of 3 to 60 g/15 mm, a pore closing start temperature of 135 to 140°C, and a pore closure maintaining upper-limit temperature of 180 to 190°C, which process comprises heat-treating a laminate film of three or more layers at a temperature of 110 to 140°C, said film having been obtained by thermocompression bonding of polypropylene and polyethylene films in an alternate manner at a temperature of 120 to 140°C, thereafter stretching the thus heat-treated film by 10 to 100% while holding the film at a temperature of 20 to 35°C, then stretching the thus-stretched film by 100 to 400% while holding the film at a temperature of 70 to 130°C, and subsequently heat-treating the thus-stretched film at a temperature higher by 5 to 45°C than the temperature of the

latter stretching step to obtain the above porous laminate film.

Further, the present invention is concerned with a process for preparing a battery separator, which process comprises heat-treating a laminate film of three or more layers, said film having been obtained by thermocompression bonding of polypropylene and polyethylene films at a temperature of 130 to 140°C, said polypropylene film having a birefringence of 10×10^{-3} to 20×10^{-3} and an elastic recovery of 80 to 94% at 100% elongation after heat treatment at 150°C for 30 minutes, and said polyethylene film having a birefringence of 20×10^{-3} to 40×10^{-3} and an elastic recovery of 20 to 50% at 50% elongation, thereafter stretching the thus heat-treated laminate film by 10 to 100% while holding the film at a temperature of -20°C to +50°C, then stretching the thus-stretched film by 100 to 400% while holding the film at a temperature of 70 to 130°C, and subsequently heat-treating the thus-stretched film at a temperature higher by 5 to 45°C than the temperature of the latter stretching step.

The gist of the present invention resides in a battery separator comprising a process laminate film obtained by stretching a laminate film of three or more alternate non-porous layers of polypropylene and polyethylene to render the film porous. The number of constituent layers of the laminate is three or more. For example, it may be four or five layers if only polypropylene layer and polyethylene layer are alternate with each other. The polypropylene and polyethylene which constitute the layers may be different in molecular weight from

one layer to another. The polypropylene preferably has a high stereoregularity, while the polyethylene is preferably a high density polyethylene, but a medium density polyethylene is also employable. The polypropylene and polyethylene may contain additives such as, for example, surfactants, antioxidants, plasticizers, flame retardants, and colorants. It is optional whether the laminate film of three or more layers is to be prepared by co-extrusion at a time or by lamination of polypropylene and polyethylene films which have been formed separately, if only the laminate film is uniform in thickness and can be made porous by stretching. However, the latter method of forming the films separately is more advantageous in point of equipment, including the film forming machine, and in view of easiness of the film forming operation. As to the film forming method, a melt extrusion method using a T-die is suitable, provided an inflation method and a wet extrusion method are also adoptable. In the case of forming each film by melt extrusion using a T-die, there usually are adopted a temperature higher by 20 to 60°C than the melting temperature of the resin used and a draft ratio of 10 to 1,000, preferably 200 to 500. The haul-off speed is not specially limited, but is usually in the range of 10 to 50 m/min. The birefringence and elastic recovery of the extruded films exert influence on the pore diameter, porosity, interlaminar peel strength and mechanical strength of the porous laminate film obtained after stretching.

The polypropylene film has a birefringence of 10×10^{-3} to 20×10^{-3} , preferably 11×10^{-3} , and exhibits an elastic recovery of 80 to 94%, preferably 84 to 92%, at 100% elongation

after heat treatment at 150°C for 30 minutes. The polyethylene film has a birefringence of 20×10^{-3} to 40×10^{-3} , preferably 25×10^{-3} to 35×10^{-3} , and exhibits an elastic recovery of 20 to 50%, preferably 25 to 40%, at 50% elongation. If the birefringence of the polypropylene film and that of the polyethylene film are outside the above ranges, respectively, it will be impossible to make them porous to a satisfactory extent, and this is also true of the case where the elastic recoveries of both films are outside the respective ranges referred to above. The thickness of each of these films, which is also related to the thickness and the purpose of use of the porous laminate film obtained after stretching for the development of porous structure, is in the range of 5 to 20 μm , preferably 10 to 15 μm .

The values of birefringence as referred to herein are values obtained under a crossed nicols using a polarizing microscope and a Berek compensator. The elastic recovery is obtained by the following formula (1) or (2). Formula (1) is for a polypropylene film, and formula (2) is for a polyethylene film. For determining the elastic recovery of a polypropylene film, a film sample of 10 mm wide by 50 mm long is mounted to a tensile strength tester at 25°C, 65% RH, after heat treatment at 150°C for 30 minutes, then is elongated up to 100% elongation at a rate of 50 mm/min, and just after the elongation the elongated sample is relaxed at the same rate. As for a polyethylene film, a film sample of 15 mm wide by 2 inches long is mounted to a tensile strength tester at 25°C, 65% RH, and is elongated up to 50% elongation at a rate of 2

inches/min, then is held in the elongated state for 1 minute and is thereafter relaxed at the same rate.

Formula (1)

$$\text{Elastic Recovery (\%)} = \frac{(\text{length at 100\% elongation}) - (\text{length at zero load after 100\% elongation})}{(\text{length before elongation})}$$

Formula (2)

$$\text{Elastic Recovery (\%)} = \frac{(\text{Length at 50\% elongation}) - (\text{length at zero load after 50\% elongation})}{(\text{length at 50\% elongation}) - (\text{length before elongation})}$$

Polypropylene film(s) and polyethylene films are laminated together by the application of heat and pressure. In laminating three films, the films are passed between heated rolls for compression bonding. More particularly, films are wound out from three raw film roll stands and are nipped between heated rolls for compression bonding to give a laminate film. It is necessary that this thermocompression bonding be carried out so as not to cause a substantial deterioration in birefringence and elastic modulus of each constituent film. Preferably, the three constituent films are laminated in such a manner that the surface and back layers are polypropylene films and the layer interposed therebetween is polyethylene film, whereby there will be obtained a porous laminate film free of curling, difficult to undergo external damage, superior in heat resistance and mechanical strength,

and meeting the characteristics required of a separator for battery such as high safety and reliability.

The temperature of the heated rolls, in other words, the thermocompression bonding temperature is preferably in the range of 120 to 140°C, more preferably 125 to 135°C. If this temperature is too low, the peel strength of constituent films is low, thus causing delamination in the subsequent stretching step. Conversely, if the temperature in question is too high, the polyethylene film will melt, thus resulting in marked

deterioration in both birefringence and elastic recovery of the film, not affording a porous laminate film that satisfies the desired characteristics. Preferably, the nip pressure is in the range of 1 to 3 kg/cm², and the wind-out speed is 0.5 to 8 m/min. The resulting laminate film preferably has a peel strength in the range of 3 to 60 g/15 mm. The thickness of the laminate film is not specially limited, but the range of 20 to 60 μ m is usually suitable.

The laminate film is heat-treated prior to stretching. The heat treatment is performed at a constant length or under application of 3 to 10% tension using an even of a heated air circulating type or a heat roll. The temperature of the heat treatment is in the range of 110 to 140°C, preferably 115 to 130°C. If the temperature is lower than this range, the laminate film will not become porous to a satisfactory extent, and a too high heat treatment temperature is inconvenient because there would occur melting of the polyethylene layer. As to the heat treatment time, 3 seconds to 3 minutes will do.

The laminate film thus heat-treated is then subjected to stretching to afford a porous laminate film. The stretching operation is preferably conducted in two steps which are a low temperature stretching step and a subsequent, high temperature stretching step. Only a single stretching step may result in the polypropylene and polyethylene layers being not made porous to a satisfactory extent, or the interlaminar peel strength being deteriorated, thus leading to debased characteristics of the resulting laminate film to be used as a separator for battery.

The low temperature stretching is performed usually by utilizing a difference in circumferential velocity between draft rolls. The temperature of the low temperature stretching is preferably in the range of -20°C to $+50^{\circ}\text{C}$, more preferably 20 to 35°C . A too low temperature is apt to cause rupture of the film being stretched, and a too high temperature will result in the film being not rendered porous to a satisfactory extent. The draft ratio in the low temperature stretching is in the range of 5 to 200% , preferably 10 to 100% . If the draft ratio is too low, there will not be attained a predetermined porosity, and a too high draft ratio will no longer make it possible to attain predetermined porosity and pore diameter. Thus, the above-mentioned range of draft ratio is suitable. In the present invention, the draft ratio in the low temperature stretching follows the following formula (3) wherein L_1 means the length of the film after the low temperature stretching and L_n means the length of the film before the same stretching:

Formula (3)

$$E_1 = [(L_1 - L_n)/L_n] \times 100$$

The laminate film after the low temperature stretching is the stretched at a high temperature. temperature. The high temperature stretching is usually performed in an oven with circulating heated air by utilizing a difference in circumferential velocity between draft rolls. No special limitation is placed on the number of the draft rolls, but it is suitable to use 7 to 14 sets of draft rolls. The temperature of the high temperature stretching is preferably in the range of 70 to 130°C, more preferably 80 to 125°C. Temperatures outside this range are not appropriate because there will not be attained a sufficient pore volume. Preferably, the high temperature stretching is conducted at a temperature higher by 40 to 100°C than the temperature of the low temperature stretching. The draft ratio in the high temperature stretching is in the range of 100 to 400%. Too low and high draft ratios will result in low and high gas permeabilities respectively. For this reason the above range is preferred. In the present invention, the draft ratio (E_2) in the high temperature stretching follows the following formula (4) wherein L_2 means the length of the film after the high temperature stretching and L_1 means the length of the film after the low temperature stretching:

Formula (4)

$$E_2 = [(L_2 - L_1)/L_1] \times 100$$

After the low temperature stretching and the high temperature stretching, the stretched film is subjected to heat treatment at a temperature higher by 5 to 45°C than the

temperature of the high temperature stretching. For example, the heat treatment is carried out by a method wherein the stretched film is subjected to heat-shrinking by 10 to 50% in length so as to prevent shrinkage of the film in the stretching direction caused by the residual stress in the stretching operations, or by a method generally called thermosetting wherein the stretched film is heat-treated while keeping the film length in the stretching direction constant. The desired porous laminate film having a high dimensional stability and a high interlaminar peel strength is obtained by this heat treatment.

The porous laminate film thus prepared according to the present invention has a porosity of 30 to 80%, preferably 35 to 60%, and a maximum pore diameter of 0.02 to 2 μm , preferably 0.08 to 0.5 μm , though both vary slightly depending on what values are selected in the foregoing manufacturing conditions. If the porosity is too low, the porous laminate film obtained will not fulfill a satisfactory function in its use as a battery separator, and a too high porosity will lead to deterioration in mechanical strength. If the maximum pore diameter is too small, the resulting porous laminate film will not be suitable for use as a battery separator or an electrolytic capacitor separator because of poor ionic movement, nor is it suitable for use in the fields of medical treatment, water treatment and air conditioning because of increase in resistance. A too large maximum pore diameter will permit ionic movement which is too large for use as a battery separator or an electrolytic capacitor separator. Further, a

too large maximum pore diameter will result in poor removal of microorganisms or virus in the water treatment field, or unsatisfactory function of the film when used as a blood plasma purifying film in the medical field.

The porous laminate film according to the present invention has a gas permeation rate of 150 to 1,500, preferably 300 to 800. In using the film as a battery separator, if the gas permeation rate is too low, the ion flow will be suppressed, while if it is too high, the ion flow will become too fast, which expedites the rate of temperature rise in the event of trouble. Further, the porous laminate film has an interlaminar peel strength of 3 to 60 g/15 mm and a curling height of less than 5 mm, preferably less than 3 mm, more preferably less than 2 mm. If the interlaminar peel strength is low, there easily occur delamination, curling and elongation of the film, for example in the battery separator manufacturing process, and thus there remains a problem in point of product quality. As to the overall thickness of the porous laminate film, an appropriate thickness can be selected is to be used, with no special limitation being placed thereon. In the case of using the film as a battery separator, an appropriate thickness thereof is in the range of 20 to 50 μm from the viewpoints of mechanical strength, performance, and reduction of size.

The following examples are given to illustrate the present invention in more detail, provided the invention is not limited thereto.

Example 1

Polypropylene (Ube Polypro F13EA, a product of Ube Industries, Ltd.) having a number average molecular weight of 70,000, a weight average molecular weight of 480,000 and a melt index of 3 was melt-extruded at 200°C using a T-die having a discharge width of 1,000 mm and a discharge lip opening of 4 mm. The discharged iflm was sent to a cooling roll held at 90°C and was cooled by applying a cooled air of 25°C. The cooled film was then taken up at a rate of 32 m/min. and a draft ratio of 366. The unstretched polypropylene film obtained was found to have a thickness of 12 μm and a birefringence of 14.7×10^{-3} . Its elastic recovery after heat treatment at 150°C for 60 minutes was 88.2%.

Separately, a high density polyethylene (Hizex 2208J, a product of Mitsui Petrochemical Co., Ltd.) having a density of 0.968 and a melt index of 5.5 was melt-extruded at 173°C using a T-die having a discharge width of 1,000 mm and a discharge lip opening of 4 mm. The discharged film was sent to a cooling roll held at 115°C and was cooled by applying a cooled air of 25°C. The cooled film was then taken up at a rate of 40 m/min. and a draft ratio of 448. The unstretched polyethylene film obtained was found to have a thickness of 11 μm and a birefringence of 27.1×10^{-3} . Its elastic recovery at 50% elongation was 29.6%.

Using the unstretched polypropylene film and unstretched polyethylene film obtained above, there was prepared a three-layer laminate film of a sandwich structure comprising polypropylene layers as two outer layers and a polyethylene layer as an inner layer in the following manner.

Two sheets of the unstretched polypropylene film and one sheet of the unstretched polyethylene were wound out from respective feed roll stands at a rate of 5.4 m/min. The unstretched films were passed through heating rolls to combine the films at a temperature of 125°C and a linear pressure of 1.8 kg/cm and were then taken up at the same rate by a cooling roll held at 50°C. The tensions applied for winding out the unstretched films were 3 kg for the polypropylene films and 0.9 kg for the polyethylene film. The resulting laminate film had a thickness of 34 μ m and a peeling strength of 16 g/15 mm.

The three-layer laminate film thus obtained was then passed through an oven with circulating heated air of 125°C for a period of 113 seconds at 5% stretching. The heat-treated film was then stretched 20% between nip rolls held at a low temperature of 35°C. The distance between the nip rolls was 350 mm and the feed roll gave a feeding rate of 1.6 m/min. The film was subsequently supplied into an oven with circulating heated air of 110°C for stretching the heated film to give total 115% stretching by utilizing a difference in circumferential speed between the rolls employed. The thus-stretched film was then heat-fixed on a heated roll of 125°C for 25 seconds to attain 16.7% relaxation. In this manner there was obtained a continuous porous laminate film.

The porous laminate film thus obtained was measured for thickness, porosity, maximum pore diameter, pore specific surface, gas permeation rate, tensile strength, tensile modulus, SD start temperature, thermal durability peeling strength, etc. The results are as shown in Table 1. The

porous laminate film was little curled and had no pinholes. A thermal shutdown behavior of the film is shown in Figure 1. Wherein the axis of ordinates is for the gas permeability (sec/100 cc) and the axis of abscissas is for the temperature (°C). The porosity, maximum pore diameter and pore specific surface were measured by a mercury porosimeter (available from Yuasa Ionic Co., Ltd.), the gas permeation rate (Gurley number) was determined in accordance with JIS P8117, and the tensile strength and tensile modulus were measured in accordance with ASTM D-822. The peel strength was determined at 25°C, 65% RH, using a strip of 15 mm wide which was in part peeled on the peel strength determining interface, and by drawing the strip at a length of 75 mm and at a rate of 500 mm/min, under T-peeling, on a tensile strength tester. The thermal shutdown behavior, SD start temperature and thermal durability were determined by the steps of mounting the film specimen to a holder of 60 mm diameter in a wholly fixed state, allowing it to stand for 1 minute within an oven with circulating heated air heated to a present temperature, taking out the heated film specimen from the oven, allowing it cool to room temperature still under the fixed condition, and measuring the gas permeability in accordance with JIS P8117. The curling height was measured by placing a strip of 20 mm wide by 100 mm long of the film on a metal plate held in a horizontal state, treating the film with a static eliminator brush lightly two or three times, allowing the film to stand for 5 minutes, and measuring the distance (D) from the central part of a line which connects both film ends bent relative to a horizontal plane and which is parallel to the horizontal plane, up to the horizontal plane.

Example 2

Polypropylene (Ube Polypro F103EA, a product of Ube Industries, Ltd.) having a number average molecular weight of 70,000 and a weight average molecular weight of 480,000 was melt-extruded at 200°C using a T-die having a discharge width of 1,000 mm and a discharge lip opening of 4 mm. The discharged film was sent to a cooling roll held at 90°C and was cooled by applying a cooled air of 25°C. The cooled film was then taken up at a rate of 32 m/min. and a draft ratio of 366. The unstretched polypropylene film thus obtained was found to have a thickness of 12 μm and a birefringence of 14.7×10^{-3} . Its elastic recovery after heat treatment at 150°C for 60 minutes was 88.2%.

Separately, a high density polyethylene (Hizex 5202B, a product of Mitsui Petrochemical Co., Ltd.) having a density of 0.964 and a melt index of 0.3 was melt-extruded at 177°C using a T-die having a discharge width of 1,000 mm and a discharge lip opening of 2 mm. The discharged film was sent to a cooling roll held at 120°C and was cooled by applying a cooled air of 25°C. The cooled film was then taken up at a rate of 35 m/min. and a draft ratio of 380. The unstretched polyethylene film thus obtained was found to have a thickness of 12 μm and a birefringence of 35.3×10^{-3} . Its elastic recovery at 50% elongation was 38.9%.

Using the unstretched polypropylene film and unstretched polyethylene film obtained above, there was prepared a three-layer laminate film of a sandwich structure comprising polypropylene layers as two outer layers and a polyethylene layer as an inner layer in the following manner.

Two sheets of the unstretched polypropylene film and one sheet of the unstretched polyethylene film were wound out from respective feed roll stands at a rate of 5.4 m/min. The unstretched films were passed through heating rolls to combine the films at a temperature of 130°C and a linear pressure of 1.8 kg/cm and were then taken up at the same rate by a rooling roll held at 50°C. The tensions applied for winding out the unstretched films were 3 kg for the polypropylene films and 0.9 kg for the polyethylene film. The resulting laminate film had a thickness of 34 μ m and a peeling strength of 7 g/15 mm.

The three-layer laminate film thus obtained was then passed through an oven with circulating heated air of 125°C for a period of 113 seconds at 5% stretching. The heat-treated film was then stretched 20% between nip rolls held at 35°C. The distance between the nip rolls was 350 mm and the feed roll gave a feeding rate of 1.6 m/min. The film was subsequently supplied into an oven with circulating heated air of 110°C for stretching the heated film to give total 115% stretching by utilizing a difference in circumferential speed between the rolls employed. The thus-stretched film was then heat-fixed on a heated roll of 125°C for 25 seconds to attain 16.7% relaxation. In this manner there was obtained a continuous porous laminate film.

The porous laminate film thus obtained was measured for thickness, porosity, maximum pore diameter, pore specific surface, gas permeation rate, tensile strength, tensile modulus, SD start temperature, thermal durability, peeling strength, etc. in the same way as in Example 1. The results of

the measurements are as shown in Table 1. As to a thermal shutdown behavior of the film, it is shown in Figure 2. The porous laminate film was little curled and had no pinholes.

Comparative Example 1

A high density polyethylene (Hizex 5202B, a product of Mitsui Petrochemical Co., Ltd.) having a density of 0.964 and a melt index of 0.3 was melt-extruded at 163°C using a T-die having a discharge width of 1,000 mm and a discharge lip opening of 4 mm. The discharged film was sent to a cooling roll held at 125°C and was cooled by applying a cooled air of 25°C. The cooled film was then taken up at a rate of 10 m/min. and a draft ratio of 120. The unstretched polyethylene film thus obtained was found to have a thickness of 38 μm and a birefringence of 31.6×10^{-3} . Its elastic recovery at 50% elongation was 41.3%.

The unstretched polyethylene film was passed through an oven with circulating heated air of 125°C for

stretching. The heat-treated film was then stretched 50% between nip rolls held at a low temperature of 35°C. The distance between the nip rolls was 350 mm and the feed roll gave a feeding rate of 1.2 m/min. The film was subsequently supplied into an oven with circulating heated air of 80°C for stretching the heated film to give 100% stretching by utilizing a difference in circumferential speed between the rolls employed. The thus-stretched film was then heat-fixed on a heated roll of 108°C for 28 seconds to attain 16.7% relaxation. In this manner there was obtained a continuous, porous, single-ply polyethylene film.

The porous film thus obtained was measured for thickness, porosity, maximum pore diameter, pore specific surface, gas permeation rate, tensile strength, tensile modulus, SD start temperature, thermal durability, etc. in the same way as in Example 1. The results of the measurements are as set forth in Table 1. A thermal shutdown behavior of the film is shown in Figure 3.

Comparative Example 2

Polypropylene (Ube Polypro F103EA, a product of Ube Industries, Ltd) having a number average molecular weight of 70,000, a weight average molecular weight of 480,000 and a melt index of 3 was melt-extruded at 190°C using a T-die having a discharge width of 1,000 mm and a discharge lip opening of 4 mm. The discharged film was sent to a cooling roll held at 90°C and was cooled by applying a cooled air of 25°C. The cooled film was then taken up at a rate of 40 m/min. and a draft ratio of 156. The unstretched polypropylene film thus obtained was found to have a thickness of 29 μm and a birefringence of 13.2×10^{-3} . Its elastic recovery after heat treatment at 150°C for 60 minutes was 92%.

The unstretched polypropylene film was then passed through an oven with circulating heated air of 150°C for a period of 113 seconds at 10% stretching. The heat-treated film was then stretched 20% between nip rolls held at 130°C. The distance between the nip rolls was 350 mm and the feed roll gave a feeding rate of 1.6 m/min. The film was subsequently supplied into an oven with circulating heated air of 130°C for stretching the heated film to give 115% stretching by utilizing a difference in circumferential speed between the

rolls employed. The thus-stretched film was then heat-fixed on a heated roll of 145°C for 25 seconds to attain 16.7% relaxation. In this manner there was obtained a continuous, porous, single-ply polypropylene film.

The porous polypropylene film thus obtained was then measured for thickness porosity, maximum pore diameter, pore specific area, gas permeation rate, tensile strength, tensile modulus, SD start temperature, thermal durability, etc. in the same way as in Example 1. The results of the measurements are as set forth in Table 1. A thermal shutdown behavior of the film is shown in Figure 4.

Comparative Example 3

A porous polyethylene film having a thickness of 8 μm , a porosity of 49% and an average pore diameter of 0.123 μm was prepared by the method disclosed in Japanese Patent Publication No. JP55-32531B. In the same way was also prepared a porous polypropylene film having a thickness of 18 μm , a porosity of 52% and an average pore diameter of 0.190 μm . Then, using a roll press, the porous polyethylene film and the porous polypropylene film were laminated and compression bonded together at 134°C to afford a porous laminate film. The porous laminate film thus obtained was then subjected to measurements in the same manner as in Example 1, the results of which are as set forth in Table 1.

Table 1

| | Example 1 | Example 2 | Comparative Example 1 | Comparative Example 2 | Comparative Example 3 |
|---|-----------|-----------|-----------------------|-----------------------|-----------------------|
| Film thickness (μm) | 31 | 31 | 30 | 25 | 25 |
| Porosity (%) | 44.6 | 44.9 | 45.6 | 44.6 | 49.5 |
| Max. pore diameter (μm) | 0.1741 | 0.1784 | 0.1776 | 0.1568 | 0.171 |
| Pore specific surface area (m^2/g) | 54 | 78 | 54 | 67 | 64 |
| Gas permeability | | | | | |
| Gurley number (sec/100cc) | 540 | 750 | 517 | 333 | 1000 |
| Tensile strength (Kg/cm^2) MD | 1000 | 1410 | 1630 | 1330 | 1770 |
| Tensile modulus (Kg/cm^2) TD | 130 | 100 | 88 | 170 | 100 |
| | 8600 | 11900 | 4600 | 5900 | 4300 |
| SV start temperature ($^{\circ}\text{C}$) | 135 | 140 | 135 | 170 | 135 |
| Pore Closure maintaining upper-limit temperature ($^{\circ}\text{C}$) | 190 | 190 | 140 | 190 | 190 |
| Peel strength (g/15mm) | 24.9 | 10.3 | - | - | 0.6 |
| Curling height (mm) | 0.5 | 1.8 | 0.5 | 0.8 | 15.5 |

[Effects of the Invention]

The porous laminate film battery separator according to the present invention has a fine and uniform pore diameter, a moderate temperature as a pore-closing start temperature, a high pore closure maintaining upper-limit temperature, a wide pore closure maintaining temperature range, a high peel strength and a high tensile modulus, can remedy the drawbacks of conventional porous laminate films, and is employed suitably as a battery separator requiring high safety, reliability and precision. According to the present invention, moreover, the said battery separator can be manufactured continuously and efficiently without variations in the quality thereof.

[Brief Description of the Drawings]

Figure 1 shows a thermal shutdown behavior of the porous laminate film prepared in Example 1 according to the present invention.

Figure 2 shows a thermal shutdown behavior of the porous laminate film prepared in Example 2 according to the present invention.

Figure 3 shows a thermal shutdown behavior of the porous, single-ply polyethylene film prepared in Comparative Example 1.

Figure 4 shows a thermal shutdown behavior of the porous, single-ply polypropylene film prepared in Comparative Example 2.

Figure 5 is a diagram explaining how to measure the curling height.

Fig. 1

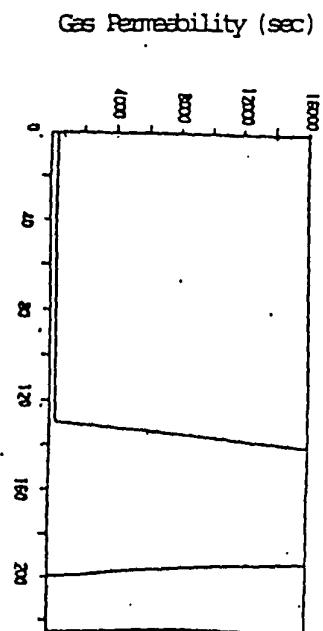


Fig. 2

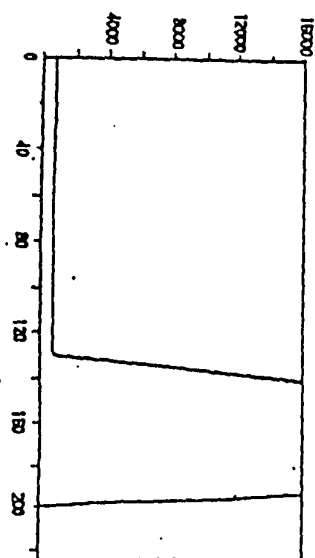


Fig. 3

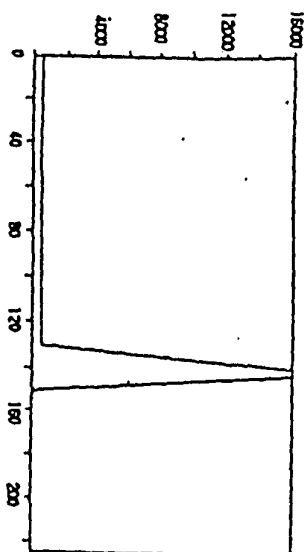
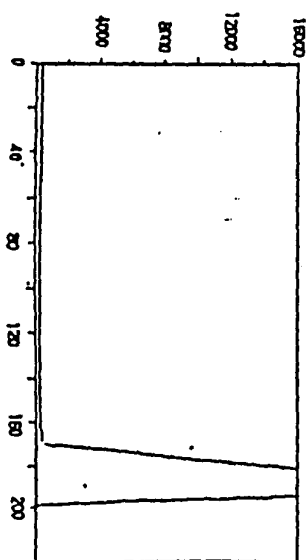


Fig. 4



5.

